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SPICES - A POTENT REPOSITORY OF ANTIOXIDANTS FOR PROCESSED FOODS – A REVIEW

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ABSTRACT

Free radicals are often produced in our body as well as food products as result of oxidation reactions. Antioxidants which could terminate these chain reactions by removing free radical intermediates and inhibit other oxidation reactions by being oxidized it selves are added to foods especially fatty foods for delaying rancidity and improving their shelf life. Antioxidants are able to prevent or inhibit oxidation processes. The protection of foods from oxygen is the basic principle upon which antioxidant protective technologies are based. Both synthetic as well as natural antioxidants are using in food industry but the application of synthetics has been reassessed due to its potential carcinogenic effects. Research is being focused on spices and its extracts which are a rich source of antioxidant compounds. Various antioxidant compounds have been isolated, many of them being phenols. Direct relationship exists between the total phenolic contents and the antioxidant activities in spices. Different antioxidant sources, their mode of action, application in food industry and antioxidant activities of garlic, black pepper, curry leaf and coriander leaves are reviewed in this paper.

KEYWORDS: Oxidation, Free Radicals, Bioactive Compounds, Phenols

INTRODUCTION

Antioxidants are the substances that are able to prevent or inhibit oxidation processes in human body as well as in food products. Oxidation is a chemical reaction that transfers electrons from a substance to an oxidizing agent. Oxidation reactions can produce free radicals, which start chain reactions that damage cells. Antioxidants terminate these chain reactions by removing free radical intermediates and inhibit other oxidation reactions by being oxidized themselves. As a result, antioxidants are often reducing agents such as thiols, ascorbic acid or polyphenols (Sies, 1997). Antioxidants have been added to frying media to improve the shelf life of deep fried snack food products (Stuckey, 1968). The protection of foods from oxygen is the basic principle upon which antioxidant protective technologies are based.

Antioxidants are grouped into primary or natural antioxidants and secondary or synthetic antioxidants.Primary or natural antioxidants are the chain breaking antioxidants which react with lipid radicals and convert them into more stable products. Antioxidants of this group are mainly phenolic in structure and include the following (Hurrell, 2003).

Antioxidant minerals, which are co-factor of antioxidant enzymes and their absence will definitely affect metabolism of many macromolecules such as carbohydrates. Examples include selenium, copper, iron, zinc and manganese. Antioxidant vitamins, which are needed for most body metabolic functions. They include-vitamin C, vitamin E, vitamin B. Phytochemicals are phenolic compounds that are neither vitamins nor minerals like, flavonoids that give vegetables fruits, grains, seeds leaves, flowers and bark their colours, catechins are the most active antioxidants in green

and black tea and sesamol and carotenoids are fat soluble colours like beta carotene, lycopene in fruits and vegetables and zeaxantin especially in spinach and other dark greens.

Secondary or synthetic antioxidantsinclude Butylatedhydroxy anisole (BHA), Butylated hydroxyl toluene (BHT), Propyl gallate (PG), metal chelating agent (EDTA), Tertiary butyl hydroquinone (TBHQ) and Nor dihydroguaretic acid (NDGA).

Noor and Augustin (2006) studied the effectiveness of antioxidants on stability of banana chips and found that chips fried in refined bleached and deodorised olein containing BHA or BHT were more stable than chips fried in RBD olein without antioxidants. BHT was more effective than BHA in prolonging the shelf life of banana chips.

MECHANISM OF ACTION OF ANTIOXIDANTS

Propagation and initiation of free radicals chain reaction can be delayed or minimized by the donation of hydrogen from the antioxidants and metal chelating agent. The major antioxidants currently used in foods are monohydroxy or polyhydroxy phenol compounds with various ring substitutions. These compounds have low activation energy to donate hydrogen. Hence, the resulting antioxidant free radical is not subjected to rapid oxidation due to its stability. Antioxidant’s free-radicals can also react with lipid free radicals to form a stable complex compound thereby preventing some of their damages.

Two principle mechanisms of action have been proposed for antioxidants. The first is a chain-breaking mechanism by which the primary antioxidants donate electrons to the free radicals present in the system, example lipid radicals. The second mechanism involves removal of ROS (reactive oxygen species) and RNS (reactive nitrogen species) initiator by quenching chain initiator catalyst (Hamid *et al*., 2010).

Antioxidants in Food Preservation

The antioxidant supplementation is a generally accepted method of prolonging the stability and storage life of food products in particular the ones including fat. Antioxidants are often added to fat containing foods in order to delay the onset or slow the development of rancidity due to oxidation. The main characteristic of an antioxidant is its ability to trap free radicals.

Antioxidants play an important role in preventing undesirable changes in flavor, nutritional quality of foods and protect the cells against tissue damage associated with various human diseases (Arai *et al*., 2000). Synthetic antioxidants such as butylated hydroxyl anisole (BHA), butylatedhydroxy toluene (BHT) and propyl gallate (PG) are widely used as food additives, but their application has been reassessed because of possible toxic or carcinogenic components formed during their degradation (Namiki, 1990). So the need for more natural and safe antioxidants got increased and several gave promising results in food industry. A recent area of interest in antioxidant research is concerned with finding effective replacements for the conventional synthetic antioxidants from among various natural plant extracts which are seen to possess antioxidant properties.

Spices as Antioxidants

Herbs and spices are added to dishes and snacks to beneficially improve the health status of the consumer without detrimental effect on flavor and taste. Spices and herbs are aromatic and pungent food ingredients with significant antioxidant activities (Suhaj, 2006). Flavours and seasonings are important considerations for snacks (Williams, 1999) and

herbs could be used as both flavouring and functional ingredients (Pszczola, 1999) in snack foods. Spices are rich in phenolic compounds. The yellow colour principle present in turmeric (*Curcuma domestica*), curcumin (Narasingarao, 2003) and capsaicin (Kakar and Iwao, 1974) in Capsicum are powerful antioxidants which prevent oxidation of oils and fats. Other active principles of spices such as, eugenol (cloves), linalool (coriander), piperine (black pepper), zingerone (zinger) and cuminaldehyde (cumin) were reported to inhibit lipid peroxidation (Kakar and Iwao, 1974).

The potential antioxidant activities of selected spices extracts on enzymatic lipid peroxidation were investigated by Sobhana and Naidu (2000) and found that water and alcoholic extract (1:1) of commonly used spices (garlic, ginger, onion, mint, cloves, cinnamon and pepper) dose-dependently inhibited oxidation of fatty acid, linoleic acid in presence of soybean lipoxygenase. They had tested the antioxidant activity of selected Indian spices, of which, cloves exhibited highest while onion showed least antioxidant activity. The relative antioxidant activities decreased in the order of cloves, cinnamon, pepper, ginger, garlic, mint and onion. Spice mix namely ginger, onion and garlic; onion and ginger; ginger and garlic showed cumulative inhibition of lipid peroxidation thus exhibiting their synergistic antioxidant activity.

Garlic as Natural Antioxidant

Organosulphur compounds in garlic like s-allylcysteine and s-allylmercaptocysteine have potent antioxidant activity (Imai *et al*., 1994). Garlic has an IC 50 value of 89.25 µg/mL (Sultana *et al*., 2010). Okada *et al*., 2005 reported that garlic has antioxidant and free radical scavenging activities and identifiable odours at low concentrations and suggested that a combination of allyl group (- $CH_2CH = CH_2$) and the – S(O)S - group is necessary for the antioxidant action of thiosulphates in garlic extracts.

The products derived from garlic such as aged garlic extract (AGE) is found to have a higher antioxidant activity in comparison with fresh and other commercial garlic supplements. This could be due to the extraction procedure followed, which tends to increase stable and highly bioavailable water soluble organosulfur compound content like s-allyl-L- cysteine and s-allylmercaptocysteine with highly potent antioxidant activity. The garlic preparation is also known to contain compounds such as stable lipid soluble allyllsulfides in the form of diallylldisulfide, diallylltrisulfide and diallyllpolysulfides which exhibit antioxidant effect (Amagase*et al*., 2001).

Durairaj*et al*. (2009) studied the stability of aged garlic extract at different temperature and revealed that antimicrobial efficacy is time and temperature dependent. At room temperature aged garlic extract exhibits maximum antibacterial efficacy for 7 days and at -20^{0}C the activity can be maintained for 90 days. Aqueous extracts of garlic were evaluated for its antibacterial activity by Saravanan et al. (2010) and observed maximum activity against *Klebsiellapneumoniae* (8mm) and minimum against *Salmonella typhii* (4mm).

Asimi*et al*., 2013 studied the antioxidant activity of some Indian spices using different methods and reported them in descending order as Cumin > Garlic > Cinnamon > Turmeric > Ginger when analysed by DPPH method, Garlic > Cumin > Turmeric > Ginger > Cinnamon by FRAP method and Turmeric > Cinnamon > Garlic > Cumin > Ginger by TPC method. Thermal stability studies on garlic (Gazzani, 1994) and crude gingerol (Eyun and Kyu, 1993), in oils (soybean and ground nut) heated at 105–165°C showed significant antioxidant activity.

Black Pepper as Natural Antioxidant

Both water and ethanol extract of black pepper exhibited strong antioxidant activity (Gulcin, 2005). Chemically pepper corn contains lignans, alkaloids, flavonoids, aromatic compounds and amides (Jirovetz*et al*., 2002). *In vitro*

antioxidant activity of white and black pepper were compared by Agbor*et al*., 2006and reported that the hydrolysed (total polyphenol) extracts of both white and black pepper had significantly higher polyphenol concentrations than the non-hydrolysed (free phenol) extracts and so black pepper had higher antioxidant activity.

Misharina*et al*., 2009 established that essential oils of garlic, clove bud, ginger and leaves of cinnamon have the maximal efficiency of inhibiting hexenal oxidation (80 –93%), while black pepper oil has the minimal (49%).

Pepper oil exhibited antioxidant activity during frying when used alone or in combination with capsaicin or alpha-tocopherol. It is suggested that red pepper seed oil can be used to avoid thermal oxidation instead of soybean oil duringdeep frying and thermal. Antioxidant potential of garlic *in vivo* and *in vitro* has been proved. Garlic is rich in selenium and organosulphur compounds, which have pronounced antioxidant activity (Hemalatha&Ghafoorunnisa, 2007).

Shiva Rani *et al*., reported that piperine showed a maximum zone of inhibition against a bacteria, *Staphylococcus aureus*(18mm) and minimum against *Escherichia coli* (8mm) and also, maximum antifungal activity against*Fusariumoxysporum*(14mm) and very least activity against *Aspergillusniger*(38mm).Pundir and Jain (2010) compared the antimicrobial activity of black pepper and turmeric extracts and found that both the extracts can be an alternative to chemical preservatives and can be used for enhancing the shelf life of food since, they found them effective against *Bacilussubtilis* and *Staphylococcus aureus*.

Curry Leaf as Natural Antioxidant

Sreeramulu*et al*., 2013 studied the natural antioxidant activity and total phenolic content of selected green leafy vegetables and reported antioxidant values ranging from 21 – 1021 mg/100g and phenolic content ranging from 77 – 1077 mg/100g, with curry leaves having the highest and spinach having the least. They found that curry leaves showed an increase in polyphenol content of 133% on conventional cooking, 109% on pressure cooking and 127% on microwave cooking.

Antioxidant protein compounds isolated from curry leaf was effective in scavenging free radicals at 150 fold lesser concentration compared to BHA and tocopherol (400 µM) (Biswas *et al*.,2006). Aqueous extract of *Murrayakoenigii* leaves (10µg/ml) inhibited 90% of lipid peroxidation (Vandana*et al*., 2012).

Oleoresin of curry leaves extracted using acetone was evaluated for its antioxidant activity using a β-carotene–linoleic acid model system. The oleoresin showed maximum activity of 83.2% at 100 ppm in comparison to a synthetic antioxidant, BHA which exhibited 90.2% activity at the same concentration. Two antioxidant compounds namely mahanimbine and koenigine were isolated from curry leaf (Das *et al*., 2011). Kale and More (2014) reported that curry leaves have high calcium content (761mg per 100g). They studied the bactericidal activity of curry leaves extracts and reported that the activity of aqueous extracts at lower concentration is intermediate and at high concentrations it is bactericidal.

Harika*et al*. (2010) reported highest antibacterial and antifungal activities of curry leaf extracts against *E. coli*bacteriawith 15±3mm zone of inhibition and for fungi *Aspergillusniger* with 14±1mm zone of inhibition. Ethanol, methanol, ethylacetate, acetone, chloroform, petroleum ether, hexane, hot water and aqueous extracts of curry leaves were tested for antimicrobial activity by Baskaran*et al*. (2011) and found that hot water extracts showed more activity against *Stephylococcusaureus* (28.17±0.29mm) and ethanol extracts showed more activity against *Aspergillusniger* and *Candida tropicalis*(12.17±0.15m).

Coriander as Natural Antioxidant

Coriander extracts contain phenolics and caroteinoids which exhibit a considerable antioxidant action (De Almedia*et al*., 2003). Coriander has an IC 50 value (58.36 µg/mL) higher than that of the ascorbic acid standard (22.78 µg/mL) as reported by Sultana *et al*. (2010).

Extracts of different polarity from leaves and seeds of coriander (*Coriandrumsativum*) and coriander oil were investigated for antioxidant activity by Wangensteen*et al*. (2004) and found that coriander leaves showed higher antioxidant activity than seeds. They suggested that addition of coriander to food will increase the antioxidant content and may have potential as a natural antioxidant inhibiting unwanted oxidation process.

Darughe*et al*. (2012) analysed chemical composition of coriander essential oil (CEO) and identified camphor (44.99%), cyclohexanol acetate (cis-2-tert.butyl-) (14.45%), limonene (7.17%), α-pinene (6.37%). Antioxidant and antifungal activities of CEO were evaluated in cake during 60 day storage at room temperature. The results indicated that, CEO at 0.05, 0.10 and 0.15% inhibited the rate of primary and secondary oxidation products formation in cake and their effects were almost equal to BHA at 0.02 % ($p<0.01$).

Sreeramulu*et al*., 2013 reported an increase in polyphenol content of 174% on conventional cooking, 188% on pressure cooking and 211% on microwave cooking. They also reported an increase in DPPH (2, 2 – diphenyl – 1 – picrylhydrazyl) activity of 81% on conventional cooking, 101% on pressure cooking and 133% on microwave cooking of coriander leaves.

CONCLUSIONS

Spices are a great repository of antioxidants. Several methods of extraction and utilization of these compounds are available for its use in food industry. Use of spices from time immemorial is still can be considered safe and ecofriendly when compared to the possible carcinogenic effects of synthetic food adulterants. The studies described in this review demonstrate the antioxidant properties of selected spicesand the active constituents which protectsfrom free radical damage. This may be useful for identifying spices that are rich in antioxidantssuited for specific food products for enhancing their shelf life and quality.

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